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MARCT

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(54) ELECTROCHEMICAL CELL

(71) We, SIEMENS ABLTIENGESELLSCHAFT, a German company, of Berlin and Munich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an electrochemical cell, in which at least one electrode comprises a composition capable of catalyzing the conversion of a hydrocarbon containing at least one hydroxyl group.

Catalytic compositions are used particularly in electrochemical cells, such as fuel elements. For a considerable time electrocatalysts containing a precious metal, such as palladium or platinum, have been used in current generators of this kind. These precious metals, as well as Raney metals, such as Raney nickel and Raney platinum, are also used to promote the chemical conversion of liquid fuels dissolved in an electrolyte, such as glycol, glycerin, methanols, saccharose or formate. The term "Raney metal" is used herein to refer to a catalytically active metal produced from an alloy of that metal and another metal, by the action of that alloy of an alkaline solution which dissolves only the other metal, thereby leaving the catalytically active metal in porous form. The electrocatalysts are generally incorporated in sintered or so-called supported electrodes (for example as described in British Patent Specification No. 1,120,591) or they are used to coat gauzes which then act as wire gauze electrodes. However, an adverse feature of the known electrocatalysts is that a relatively rapid ageing, i.e. a reduction in activity is noticeable; moreover, Raney nickel displays low activity after ageing and high susceptibility to corrosion.

According to the present invention, there is provided an electrochemical cell in which at least one electrode comprises a composition capable of catalyzing the conversion of a hydrocarbon containing at least one hydroxyl group, which composition comprises one or both of platinum and palladium, and also bismuth, the bismuth content of said composition being in the range from 0.5 to 70% by weight, relative to the total weight of the composition.

In an electrochemical cell of the present invention, liquid reactants dissolved in the electrolyte, i.e. fuels, may be converted with high current densities at negative potentials. In comparison with pure platinum, the catalytic composition shows considerable increased activity during the transformation in this case, anodic oxidation of fuels such as glycol, methanol, glycerin, saccharose and formate. High current densities may be achieved in an electrochemical cell according to the present invention, particularly when the composition is used in the form of wire gauze electrodes. Wire gauze electrodes have a large surface area which ensures good accessibility to the electrode for the fuel, i.e. good supply of fuel to the electrode. Advantageously, electrodes in the form of groups of wire gauze with gauzes of different mesh size may be used. Tests which we have conducted indicate that the composition has a reduced ageing rate in comparison to platinum, for instance.

An electrochemical cell according to the present invention can be used to determine the concentration of hydrocarbons containing hydroxyl groups, particular sugars. Such a cell could include a working electrode which comprises the catalytic composition, and a counter electrode. Tests have shown that in an electrochemical cell according to the invention, high conversion rates can be achieved and that saccharose, for instance, can be converted within a wide potential range with constant current

density. A corresponding sugar sensor, furthermore, indicates already low saccharose concentrations, i.e. from approximately 10^{-3} mol/l (corresponding to 0.034% by weight).

As indicated above, the content of bismuth in the composition is in the range from 0.5 to 70% by weight, relative to the total weight of the composition. Advantageously, the composition may contain intermetallic compounds of platinum and/or palladium with bismuth, particularly the intermetallic compound PtBi. The compound PtBi has a bismuth content of 51.7% by weight. A further intermetallic compound, for instance is Pd₃Bi with a bismuth content of 39.6% by weight.

The composition may also include lead.

The present invention also provides an electrochemical cell in which an anode comprises the aforementioned composition. Catalytic compositions of this type are similarly characterised by high activity, their resistance to ageing being generally adequate.

The present invention will now be illustrated by the following embodiments.

To produce wire gauze electrodes, nickel gauzes were used with a mesh size of 0.19 mm, a wire thickness of 0.13 mm, and a gauze thickness of 0.3 mm. These gauzes were degreased by means of an appropriate solvent, in this case acetone, and were treated with hydrochloric acid (approx. 18%) to remove the surface oxide layer. The desired metals were then deposited without current on circular gauzes with a diameter of approximately 40 mm, i.e. a surface area of approximately 12 cm². For thus purpose, the gauzes were immersed in a dip solution containing the appropriate metal salts.

To produce wire gauze electrodes containing platinum and bismuth, a solution was used which was produced as follows. 75 Millilitres of an aqueous solution of hexachloroplatinic (VI) acid H₄[PtCl₆] with a platinum content of 3.9% by weight were diluted with 5% HNO₃, to give 1 litre. From this solution with a platinum content of circa 2.9 grams were taken a number of samples approximately 5 ml in each case, i.e. quantities containing about 15 mg platinum. Each of these platinum salt solutions was mixed with one of various aqueous solutions of bismuth (III) nitrate with different bismuth contents, and was diluted with water to give ca. 50 ml. The nickel gauzes were then dipped into these solutions.

In order to produce dip solutions which contain palladium as well as bismuth and platinum, 42.5 ml hexachloroplatinic (VI) acid solution with 5% HNO₃ was diluted to 1 litre, and 2.1 g PdCl₂ was dissolved in it. From this solution, containing ca. 1.65 g platinum and 1.25 g palladium, were taken 5 ml aliquots which contained approximately 15 mg precious metals, which were mixed with one of different bismuth (III) nitrate solutions and diluted with water to 50 ml.

Dip solutions which, in addition to platinum, palladium and bismuth, contained lead, were produced by dissolving 7.5 g lead acetate, Pb(CH₃COO)₂ · 3H₂O, in the nitric acid solution of hexachloroplatinic (VI) acid and palladium chloride. From this solution, which contained ca. 1.65 g Pt, 1.25 g Pd and 4.1 g Pb, were then taken aliquots of approx. 2 ml with a total metal content (Pt+Pd+Pb) of ca. 15 mg, which were mixed with one of different bismuth salt solutions and diluted with water to 50 ml.

The gauzes were immersed in the dip solutions until the metals had been completely precipitated. This took about 5 to 10 minutes and may be recognized by the fact that the originally yellowish brown solution became colourless or took on a slightly greenish tinge. This results in 15 mg of the metals, i.e. Pt or Pt+Pd or Pt+Pd+Pb, corresponding to a deposit of 1.25 mg/cm², as well as specific amounts of bismuth being found on the gauzes of area of 12 cm².

Test results obtained with wire gauze electrodes of this type during the transformation of glycol are illustrated graphically in Figures 1 to 3 of the accompanying drawings, in which the current density, i, is plotted in mA/cm² on the ordinate and the potential, e, in mV on the abscissa, measured against an Hg/HgO reference electrode in 6M KOH. 6M KOH, having a content of 2M glycol, served as the electrolytic liquid; the electrolyte temperature was ca. 60°C.

Figure 1 shows measurement results obtained with electrodes containing only platinum and bismuth, apart from one control. The curves 10 to 13 correspond to electrodes with the composition set out in the following Table 1.

TABLE 1

Curve	Quantity (in mg) of catalytic metals in dipping solution			Quantity (in mg/cm ²) of catalytic metals deposited		
	Total	Pt	Bi	Total	Pt	Bi
10	15.0	15.0	—	1.250	1.25	—
11	15.2	15.0	0.2	1.267	1.25	0.017
12	15.4	15.0	0.4	1.283	1.25	0.033
13	15.8	15.0	0.8	1.317	1.25	0.067

It is clear from Figure 1 that the activity of the composition employed in the cell according to the present invention increases as the bismuth content increases.

Represented in Figure 2 are the results which were obtained with electrodes containing all three of platinum, palladium and bismuth, apart from one control curve 20. Curves 20 to 25 characterise electrodes having the composition set out in the following Table 2.

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TABLE 2

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Curve	Quantity (in mg) of catalytic metals in dipping solution			Quantity (in mg/cm ²) of catalytic metals deposited		
	Total	Pt+Pd	Bi	Total	Pt+Pd	Bi
20	15.0	15.0	—	1.250	1.25	—
21	15.2	15.0	0.2	1.267	1.25	0.017
22	15.4	15.0	0.4	1.283	1.25	0.033
23	15.8	15.0	0.8	1.317	1.25	0.067
24	16.6	15.0	1.6	1.383	1.25	0.133
25	18.2	15.0	3.2	1.517	1.25	0.267

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Similarly, it may be inferred from Figure 2 that with an increasing bismuth content, the activity of the composition used in the cell according to the present invention rises. Otherwise, there are no essential differences between a catalyst containing platinum, palladium and bismuth and a catalyst containing platinum and bismuth.

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The results obtained with electrodes containing lead in addition to platinum, palladium and bismuth, i.e. with electrodes in which the bismuth is partially replaced by lead, are shown in Figure 3, which also shows the results for a control containing no bismuth, curve 33. The compositions of the electrodes are set out in the following Table 3.

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TABLE 3

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Curve	Quantity (in mg) of catalytic metals in dipping solution			Quantity (in mg/cm ²) of catalytic metals deposited		
	Total	Pt+Pd+Pb	Bi	Total	Pt+Pd+Pb	Bi
30	15.4	15.0	0.4	1.283	1.25	0.033
31	15.2	15.0	0.2	1.267	1.25	0.017
32	15.1	15.0	0.1	1.258	1.25	0.008
33	15.0	15.0	—	1.250	1.25	—

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As may be seen from curves 30 to 32 in Figure 3, when the absolute lead content (and indeed the absolute lead content of Pt+Pd+Pb) is constant, the activity of the composition used in the cell according to the present invention increases as bismuth content falls. Also, but this is not shown in Figure 3, the activity increases when the lead content rises, all other factors remaining constant. From curve 33 may be inferred the fact that electrodes in which the bismuth is completely replaced by lead show an even higher activity, but such electrodes do suffer from one considerable disadvantage, namely that, as the lead content increases, the resistance to ageing of the electrodes decreases.

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In Figure 4 of the accompanying drawings are reproduced long duration tests, from which may be seen the differing resistance to ageing. Here the current density, i , is plotted on the ordinate in mA/cm² with a constant electrode potential, ϵ , of -750 mV, measured against an Hg/HgO reference electrode, and the time t is plotted on the abscissa in hours. 6M KOH having a content of 2M glycol served as the electrolytic liquid; the electrolyte temperature was 60°C. The electrodes used for the long duration tests each consisted of five of the one type of coated gauzes described

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above with a surface area of 12 cm², laid one on top of the other and held together to form an electrode package.

Curve 40 shows the results obtained with an electrode having a deposit of Pt, Pd and Bi with a precious metal content of 75 mg and a bismuth content of 14 mg. The coated electrode was approximately equivalent to the electrode used to give the curve 25 in Figure 2. In curve 41 are shown results obtained with an electrode having a deposit of Pt, Pd and Pb; the electrode had a precious metal content of 32.2 mg and a lead content of 42.8 mg and was thus approximately equivalent to the electrode used to give curve 33 in Figure 3. Comparison of curves 40 and 41 shows that the electrode with a coating of a catalytic composition according to the present invention (Pt+Pd+Bi) aged far less than an electrode with platinum, palladium and lead as above: the current density of the electrode with the coating containing bismuth after 180 hours of operation was approximately eight times that of the electrode with the coating containing lead, although the latter initially showed a higher activity.

Results of potentiodynamic measurements, i.e. measurements of current density during which the potential is varied at a uniform rate, on smooth electrodes with composition of platinum and bismuth are reproduced in the following Table 4. To produce the composition, platinum and bismuth in varying amounts were melted together at temperatures in the range of approximately 1500 to 1800°C. After cooling, the electrodes were provided with means for collecting current and their surfaces polished. The activity, which is equivalent to the current density, of the electrodes was determined by the transformation of glycol present as a 0.2M solution in 6M KOH at 60°C.

TABLE 4			
	Metal Content (% by weight)	Pt	Maximum Current Density (mA/cm ²)
	Bi		
30	100	0	8.4
	95	5	30
	90	10	50
	85	15	70
	80	20	80
	50	50	78
35	30	70	50

From Table 4 it can be seen that the maximum activity of the Pt/Bi catalytic composition varies with the composition and is high where the weight ratio of Pt:Bi is 1:1, i.e. for a composition corresponding to the intermetallic compound PtBi.

As already mentioned, the electrochemical cell according to the present invention may be used to determine sugars. Thus, with Pt/Bi catalysts in potentiodynamic measurements, for instance, even with very low saccharose concentrations, anodic currents arise which are suitable for determining saccharose content.

An electrochemical cell according to the present invention could be formed as a measuring cell as described in British Patent Specification 1,286,298. In this, a fixed diffusion zone is used, two electrodes are separated from one another by a membrane, and a diffusion limiting current serves to determine the concentration. A process of this kind is possible because high conversion rates are obtained with the composition in an electrochemical cell according to the invention. Since the transformation of saccharose takes place within a wide potential range with constant current density, a measuring cell described in British Patent Specification 1,263,544 may instead be used to determine concentration. This measuring cell similarly contains two electrodes one of which has a polarisation resistance dependent on the concentration of the dissolved reactant. However, arrangements which have three electrodes—reference, counter- and working electrodes—may also be used.

WHAT WE CLAIM IS:—

1. An electrochemical cell, in which at least one electrode comprises a composition capable of catalyzing the conversion of a hydrocarbon containing at least one hydroxyl group, which composition comprises one or both of platinum and palladium, and also bismuth, the bismuth content of said composition being in the range from 0.5 to 70% by weight, relative to the total weight of the composition.
2. An electrochemical cell as claimed in Claim 1, in which the composition contains an intermetallic compound of bismuth with one or both of platinum and palladium.

3. An electrochemical cell as claimed in Claim 2, wherein the intermetallic compound is PtBi.
4. An electrochemical cell as claimed in Claim 2, wherein the intermetallic compound is Pd,Bi.
5. An electrochemical cell as claimed in any of the preceding claims wherein the composition also contains lead.
6. An electrochemical cell as claimed in any one of the preceding claims, wherein an anode comprises said composition.
7. An electrochemical cell as claimed in any one of the preceding claims, for determining the concentration of sugar, the cell including a working electrode which comprises said composition, and a counter electrode.
- 10 8. An electrochemical cell as claimed in Claim 1, substantially as hereinbefore described.

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 Sheet 1

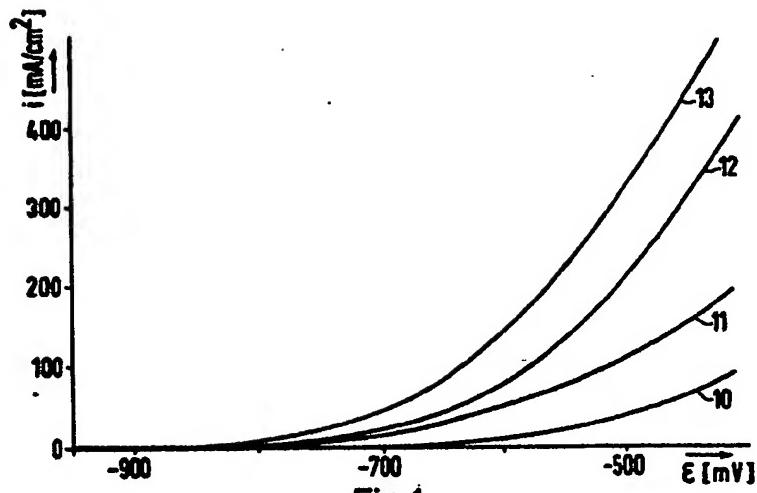


Fig.1

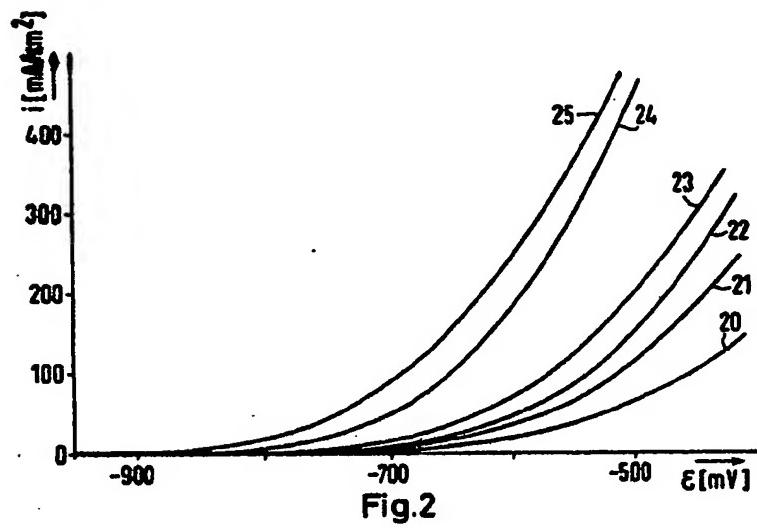


Fig.2

1559700

COMPLETE SPECIFICATION

2 SHEETS

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Sheet 2

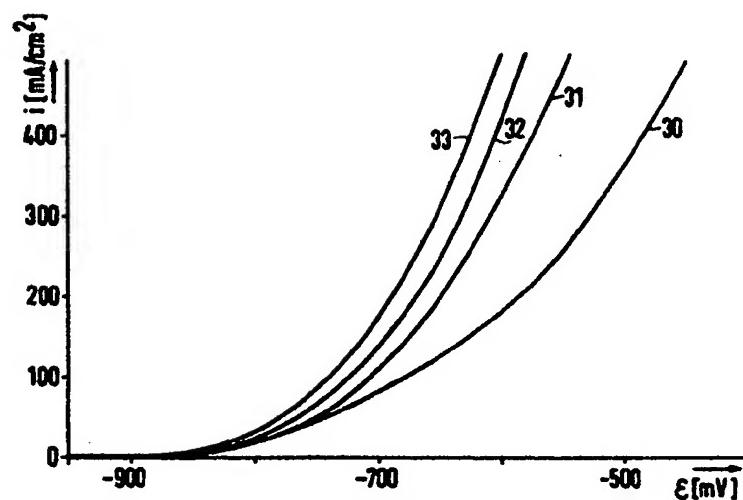


Fig. 3

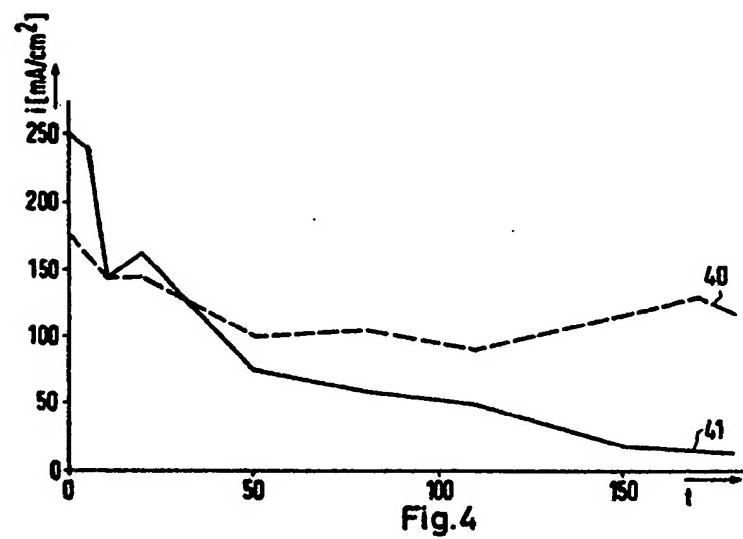


Fig. 4